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(54) Multilayer Polymer Hose or Pipe

ABSTRACT
This invention relates to a multilayer polymer hose or pipe that includes at least one layer of polyester barrier that acts as a barrier against fuels. The ideal embodiment of the hose or the pipe of this invention involves an inner polyamide protective layer, an outer polyamide protective layer, an adhesive accelerator layer between the barrier and the inner protective layer, and another adhesive layer between the barrier and the outer protective layer.

REPRESENTATIVE DIAGRAM
Diagram 1

SPECIFICATIONS
[Title of the Invention]
Multilayer polymer hose or pipe

[Brief Description of the Diagrams]
Diagram 1 is a graph displaying the transmissivity of various polymer films against FAM A, MA 35 pure methanol, tested using DIN 51604A.

[Detailed Explanation of the Invention]
This invention relates to the hose or the pipe that consists of multiple layers of polymers and shows an improved barrier effect against fuels.

Abundant information is available on polymer pipes and soft tubes, which are frequently used for cooling and breaking fluids as well as for fuel lines. In particular, fuel lines made using polyamide (in particular, polyamide 11 and polyamide 12) have been examined in "Kunststoffe und Elastomers in der Praxis (Plastics and Elastomers in Practice)" published by W. Kohlhammer, Stuttgart-Berlin-Koln-Mainz (1985).

The problem of these pipes is that their transmissivity against normal fuels is unsatisfactory, particularly considering the recent environmental and safety concerns. Another problem of these pipes is that the polymer tends to absorb some components of the fuels, causing the pipe to expand and changing the length of the pipe.

Due to these reasons, various researches have been conducted to improve the so-called mono-pipes, which consist of a single, uniform layer of polyamide 11 or polyamde 12, and made it possible to switch to polymer multilayer pipes that have a layer of polymer barrier.

DE 35 10 395 C2, DE 38 27 092 and EP 428 834 A2 introduced fuel lines that have an ethylene/vinyl alcohol co-polymer barrier layer. However, an ethylene/vinyl alcohol co-polymer with desirable barrier characteristics is extremely fragile, and very difficult to repair when they break. Due to these reasons, these polymers were only usable when they are extremely thin. Additionally,

during the press molding process, and particularly if press molded together with a thermoplastic polymer, these polymers lose their stability when the temperature reaches 220°C or above, meaning that the polymers start to fuse together, resulting in gel molecules. When this type of ethylene/vinyl alcohol co-polymer is developed into a thin film, gel molecules are immediately verifiable, and may prompt a purchaser to reject the product on visual and psychological grounds. Gel molecules are not visible if used in dyed thick-wall pipes, but the quality deteriorates, and such pipes require extremely strict quality assurance measures.

DE 38 21 723 C1 offers a three-layered pipe that has a continuous polyolefin inner coating and a polyamide outer protection layer. Based on this document and the results of the transmissivity tests, it appears that polyolefin is an excellent barrier against alcohol, and that polyamide is a good barrier against hydrocarbons. However, fuels for regular vehicles combine hydrocarbons and alcohol.

As shown in the Attached Diagram 1, the barrier value of a single polymer ingredient is not applicable to a mixed fuel. Furthermore, the transmissivity problem cannot be solved by simply putting layers of polymers that each would act as an effective barrier against one particular fuel component. Although fluoro-polymers can be used as a barrier, these polymers are not only very expensive, but also difficult to process and dispose. Additionally, when using the co-extrusion process, they do not easily compound.

Accordingly, the objective of this invention is to provide a hose or a pipe that does not have the above described weaknesses, is environmentally friendly and safe, and has low transmissivity.

The invention will be described in detail below.

The inventors of this invention, amazingly, discovered that polyester has excellent barrier characteristics against automobile fuel. This barrier effect is higher than what can be foreseen by using pure hydrocarbons, pure alcohol, or their compounds, and the barrier effect is present through a relatively wide range of alcohol concentration rates.

This invention is a multilayer polymer hose or a pipe with at least one polyester barrier layer that shows the barrier effect.

A multilayer hose or pipe made pursuant to this invention has the following advantages:

1. Polyester used to form the barrier layer is very easy to process, and polybutylene terephthalate has a superior specificity.

2. The excellent barrier characteristics of polyester, in particular of polybutylene terephthalate, against normal automobile fuels; these characteristics are superior to ethylene-vinyl alcohol co-polymer, and the cost of the materials is less.

A more detailed description of this invention, which has those characteristics, is as follows:

The most well-known polyesters used in this invention are polyethylene terephthalate (PET), polybutylene terephthalate (PBT), and polyethylene naphthanoate (PEN). As a polyester-formant, terephthalic acid and isophthalic acid should be added. Also, polyethylene softener with segment block co-polyether may be used.

The multilayer design of this invention means it benefits from the lower hydrolysis rate of polyester compared to polyamide 11 or polyamide 12. Similarly, using a multilayer pipe with at least one polyester-based barrier layer and at least one polyamide protective layer resolves the low shock tolerance characteristics of PET or PBT. The reason why this is necessary is because unimproved PET or PBT pipe cannot pass the SAE J 844 low-temperature shock test.

Normally, polyester and polyamide do not compound in a stable manner. Hence, the use of adhesive accelerators is recommended. As a proper accelerator, a thermoplastic polymer that thermodynamically shows at least partial compatibility to polyester and polyamide should be used. Polyurethane-type accelerators that include polyether and polyester urethane are particularly appropriate. Similarly, polyether polyamide types, polyether ester polyamide types, polyether ester ether polyamide types or polyamide elastomer, which is similar to those components, may be used.

Other potential adhesive accelerators include polymers that possess functionality that react to polyester and polyamide. These include polyethylene types, maleic anhydride (MA) such as polypropylene and grafted polyolefin types and co-polyolefin grafted with MA, for example, styrene-butadiene-styrene block co-polymer or styrene-(ethylene-co-butylene)-styrene block co-polymer (Shell's Kraton G). Besides MA, dibutyl maleic anhydride or acrylic acid may be used for grafting. Additionally, polymer-types that have been functionalized via epoxide equipment are effective adhesive accelerators, and may be used to accelerate the reaction described above.

The protective layer for the hose or pipe of this invention, ideally, should use polyamide. For polyamide, an aliphatic lactam with 4 to 44 carbon atoms, a condensation polymer of omega-amino carboxylic acid or an aromatic condensation polymer of omega-amino acid with 6 to 20 carbon atoms may be used.

Also, a polymer of at least one of dicarboxylic acids and at least one of diamine with 2 to 44 carbon atoms each may be used. Examples of these diamines include: ethylene diamine, 1,4-diaminobutane, 1,6-diaminohexane, 1,10-diaminodecane, 1,12-diaminododecane, meta- and para-xylylenediamine, cyclohexyl dimethylamine, bis-(p-aminocyclohexyl)-methane and their low class alkaline derivatives.

Also, examples of dicarboxylic acids include: succinic acids, glutaric acids, adipic acids, pimelic acids, suberic acids, azelaic acids, dodecanedicarboxylic acid, 1,6-cyclohexanedicarboxylic acid, isophthalic acid and naphthalenedicarboxylic acid.

PA 6; PA 11; PA 12; PA 12, 12; PA 10, 12; PA 6, 12; PA 6, 9; PA6, T; PA 6, I; PA 12, T; PA 12, I and PA 12/6, T and the homo-polyamide types and co-polyamide types of their mixtures are particularly suitable.

The polyamide types for this invention will include normal additives, such as additives that provide improved stability against UV, heat or crystallization, plasticizers, fire retardants, lubricants, inorganic fillers, and additives that improve the electric conductivity. As one of the possible embodiments, the outer protective layer may be made of polyethylene terephthalate or the inner protective layer may be made of polyolefin, or ideally, an improved polyolefin that has functionality.

This invention has a lower transmissivity value than a multilayer pipe that includes poly-vinyl alcohol as the barrier layer. This fact is clearer for gasoline mixtures containing alcohol. This pipe is chemically stable against generally used fuels, motor oils and acids used for automobile parts, and is also chemically stable against de-icing salts, in particular, zinc chloride. Hoses and pipes made pursuant to this invention are durable against the oxidation process caused by corrosive fuels (fermentation gas), and are stable against high temperatures and radiation. They show excellent shock resistance characteristics in low temperatures, satisfying the SAE J 844 shock test conducted at -40°C. Their puncturing pressure value also meets the standards for gasoline pipes. Because these pipes are malleable through heat, it is also possible to shape them in complex geometrical forms.

Various embodiments of the inner to outer layers are provided below:

PA / PUR / PBTPA / PUR / PBT / PUR / PAPBT / PUR / PAPO / grafted PO / PA / PUR / PBTPO / PBTPO / PBT / PUR / PA in the above chart, PA is Polyamide, PUR is polyurethane, PBT is polybuthylene terephthalate, and PO is polyolefin. The ideal embodiment of the hose or the pipe made pursuant to this invention would have three to five layers made of polyamide, ideally PA 12, inner part and/or outer protective layers and polybutylene terephthalate barrier layers. This includes an adhesive accelerator layer (ideally, polyurethane adhesive accelerator layer) for each polyamide layer. In the most ideal embodiment, due to the barrier effect against each fuel component, the barrier layer should also double as the inner layer.

There is no necessary limit to the total thickness of the pipe or the hose that is made pursuant to this invention, but the following would be proper.

Thickness of the protective layer: 0.2 to 0.6 mm

Thickness of the barrier layer: 0.2 to 0.7 mm

Adhesive accelerator layer: 0.05 to 0.3 mm

Particularly advantageous model uses a barrier layer that is up to 2.0 mm thick, if there are no complications in the production and in use. However, because of the improved barrier effect of the hose or the pipe made pursuant to this invention, it is more acceptable to produce thin layers, which in turn may mean that the cost of production may be higher [sic] than the pipes made pursuant to the conventional technology.

Also, if possible, the walls of the hose or the pipe may be made to bear ring grooves or screw grooves, and the protective layer may be made with antistatic finishing or anti-shock characteristics. Also, conventional plasticizers and other additives may be used to improve certain characteristics. The length may be stabilized by adding glass or other similar fibers.

The following materials and tests were actually used:

Polybuthylene terephthalate; GRILPET XE 3060 (EMS-CHEMIEAG) polyester urethane: DESMOPAN 588 (Bayer AG) plasticized PA 12: GRILAMID L25W40X (EMS-CHEMIE AG) plasticized PA 6: GRILON R47HW (EMS-CHEMIE AG) Poly-vinyl alcohol: EVAL Ec-F adhesive accelerator PP, grafted MSA: XE 3153 (EMS-CHEMIE AG) polypropylene: Novalen 1300E low-density polyethylene: Dow 150L15: grilamid PA 12 Natural PA 6: GRILON F 40 Natural MXDA 6: polyamide based on m-xylylenediamine and adipic acid (Mitsubishi Kasei Chemical). Transmissivity measurements were conducted using a dynamic measuring device at 60 °C and under 4 bars' pressure. This invention was tested under DIN 51604 B using FAM B. This FAM B consisted of 42.25% toluene, 25.35% isooctane, 12.68% diisobutylene, 4.23% ethanol, 15% methanol and 0.5% water. All the percentages here refer to the volume %.

Additionally, M35 was tested. The results in $g/m^2/h$ proved the superiority of polybuthylene terephthalate among XE 3060 (Comparative Embodiment 3) types and multilayer structures (Examples of Embodiment 1 and 2). Fuel FAM A, M35

(Haltermann Normbenzin and methanol 35 volume %) and methanol were used to test the transmissivity on 50 μm films pursuant to DIN 5160A. FAM A is a mixture of 50% toluene, 30% isooctane, 15% diisobutylene and 5% ethanol. Here, all percentages refer to the volume %.

[Example of Embodiment 1] The present Example of Embodiment pipe has a XE 3060 inner layer with the thickness of 0.6 mm. The middle layer is Desmopan 588 and its thickness is 0.1 mm. The outer layer is L25W40X (PA 12), and its thickness is 0.3 mm. The diameter of the whole pipe is 8 mm.

[Example of Embodiment 2] The thickness of the inner layer is 0.3 mm and consists of L25W40X (PA 12). The middle layer is Desmopan 588, and its thickness is 0.1 mm. The outer layer is XE 3060, and its thickness is 0.6 mm. The diameter of the whole pipe is 8 mm. Fundamentally, the inner layer of Example of Embodiment 1 is the outer layer of Example of Embodiment 2, and the outer layer of Example of Embodiment 1 is the inner layer of Example of Embodiment 2.

[Comparative Embodiment 1] Single component pipe made of L25W40X, whose diameter is 8 mm and thickness is 1 mm.

[Comparative Embodiment 2] This embodies Germany Patent Number 35 10 395. The total thickness of the five layers is 1 mm, and its diameter is 8 mm. From inside to outside, the layers are: R47HW (PA 6), 0.45 mm thick; EVAL Ec-F, 0.15 mm thick; R47HW, 0.05 mm thick; XE 3153, 0.05 mm thick; and L25W40X (PA 12), 0.3 mm thick.

[Comparative Embodiment 3] A single component pipe made of XE 3060, whose diameter is 8 mm and thickness is 1 mm.

The transmissivity of the above Examples of Embodiment were measured and their results posted in the Chart 1, which is as follows:

[Chart 1] Transmissivity (g/m²/h) Transmissivity (g/m²/h) FAM B HALTERMANN/35% methanol Example of Embodiment 1 1.1 1.1

Example of Embodiment 2 2.1 2.2

Comparative Embodiment 1 22.8 33.0

Comparative Embodiment 2 5.1 5.6

Comparative Embodiment 3 0.8 1.4

The numbers shown in specific Examples of Embodiment of this invention are merely listed for clarification, and notwithstanding those numbers, the Scope of Patent Claims of this invention attached here may be broadly interpreted and are not limited by anything outside of them.

(57) SCOPE OF CLAIMS

Claim 1
A multilayer polymer hose or pipe that shows the barrier effect and has at least one polyester barrier layer, at least one polyamide protective layer, and at least one polyurethane adhesive accelerator layer between the abovementioned polyester and polyamide.

Claim 2
As to Claim 1, a multilayer polymer hose or pipe whose abovementioned polyester is selected from the following components: polybutylene terephthalate, polyethylene naphthalate, and a mixture of these components.

Claim 3
As to Claim 1, a multilayer polymer hose or pipe whose abovementioned polyamide is selected from the following components: PA 6; PA 11; PA 12; PA 12, 12; PA 10, 12; PA 6, 12; PA 6, 9; PA 6, T; PA 6, I; PA 12, T; PA 12, I and PA 12/6, T and any mixture of these components.

Claim 4
As to Claim 1, a multilayer polymer hose or pipe whose abovementioned polyurethane is selected from urethanes, polyester urethanes and their mixtures.

Claim 5
As to Claim 1, a multilayer polymer hose or pipe whose abovementioned barrier layer is an inner layer.

Claim 6
As to Claim 1, a multilayer polymer hose or pipe that has at least one polyamide inner protective layer or at least one polyamide outer protective layer, and has a barrier layer made of polybutylene terephthalate, and whose abovementioned adhesive accelerator layer is placed between the abovementioned polyethylene terephthalate layer and the abovementioned protective layer.

Claim 7
As to Claim 1, a multilayer polymer hose or pipe that has three layers: a layer made of polybutylene terephthalate, a protective layer made of polyamide, and an adhesive accelerator layer between them.

Claim 8
As to Claim 1, a multilayer polymer hose or pipe that has five layers: an inner and an outer layer made of polyamide, a polybutylene terephthalate barrier layer between those two layers, one adhesive accelerator layer between the aforementioned inner layer and the aforementioned barrier layer, and another adhesive accelerator layer between the aforementioned barrier layer and the aforementioned outer layer.

DIAGRAM

Diagram 1